A New Preparative Method for (*E*)-2,3-Diarylbut-2-enedials

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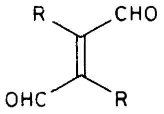
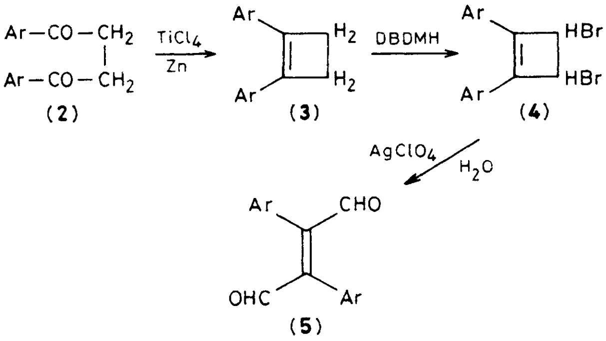
Reaction of 1,2-diaryl-3,4-dibromocyclo-but-1-enes (**4**) with silver perchlorate in the presence of water gave (*E*)-2,3-diarylbut-2-enedials (**5**), which when treated with acid were converted into 2,3-diarylbut-2-en-4-olides (**6**).

Although but-2-enedial (**1a**)[1] and its 2,3-dialkyl derivative (**1b**)[2] are known, no 2,3-diarylbut-2-enedials (**5**) have been reported. We have prepared compounds (**5**) by treating the 1,2-diaryl-3,4-dibromocyclobut-1-enes (**4**) with silver perchlorate in the presence of water. The butenes (**4**) were easily obtained by reductive cyclisation of the 1,4-diarylbutane-1,4-diones (**2**) followed by bromination.

When 1,4-diphenylbutane-1,4-dione (**2a**) was treated with $TiCl_4$–Zn[3] in tetrahydrofuran (THF) under N_2 at 50—60 °C for 24 h, 1,2-diphenylcyclobut-1-ene (**3a**) was obtained as colourless needles in 87% yield, m.p. 56 °C. By the same method, the 1,4-di(*p*-chlorophenyl) derivative (**2b**), m.p. 101—102 °C, and the 1,4-di(1-naphthyl) derivative (**2c**), m.p. 110—112 °C, were obtained in 71 and 88% yields, respectively. Treatment of (**3a**), (**3b**), and (**3c**) with 3 mol of *N,N'*-dibromodimethylhydantoin (DBDMH) in CCl_4 at 50—60 °C for 12 h gave their dibromo derivatives (**4a**), m.p. 120—121 °C, (**4b**), m.p. 140—142 °C, and (**4c**), m.p. 227—228 °C, in 89, 39, and 88% yields, respectively. The *trans*-structure of (**4a**) was determined by comparing its physical data with those of an authentic sample prepared by bromination of 3,4-dihydroxy-1,2-diphenylcyclobut-1-ene.[4]

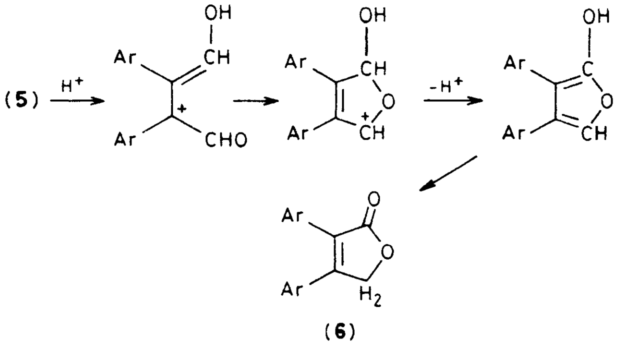


(**1**) **a**; R = H
b; R = alkyl



a; Ar = Ph
b; Ar = *p*-Cl-C_6H_4–
c; Ar = 1-naphthyl

Reaction of (**4a**) with silver perchlorate (practical grade of 90% purity, Wako Pure Chemical Industries Ltd., Japan) in THF containing water (10%) at room temperature for 10 min gave 2,3-diphenylbut-2-enedial (**5a**) as yellow needles in 80% yield, m.p. 221—222 °C, ν(CO) 1680 cm^{-1}, λ_{max} 317 (ε 9700)

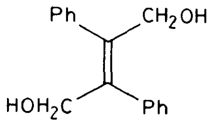


Scheme 1

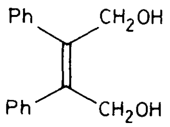
and 408 nm (1700), δ(C*H*O) 10.00.[†] Similar treatment of (**4b**) and (**4c**) with silver perchlorate gave (**5b**), m.p. 199—200 °C and (**5c**), m.p. 209—210 °C, in 80 and 95% yields, respectively. The mechanism of the reaction is not clear.

2,3-Diarylbut-2-enedials are useful materials for the preparation of various compounds because they contain two formyl groups and one double bond. For example, treatment of (**5a**) with HCl gas in $CHCl_3$ at room temperature for 1 h gave 2,3-diphenylbut-2-en-4-olide (**6a**)[5] as colourless needles in 92% yield, m.p. 119—120 °C, ν(CO) 1745, ν(C=C) 1645 cm^{-1}, λ_{max} 288 nm (ε 13 500), δ(CH_2) 5.09. Similar treatment of (**5b**) and (**5c**) gave (**6b**), m.p. 119—120 °C, and (**6c**), m.p. 176—178 °C, in 75 and 78% yields, respectively. A plausible reaction mechanism for the formation of (**6**) is shown in Scheme 1.

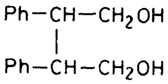
The (*E*) structure of (**5**) was determined from the following experiments. Reduction of (**5a**) with sodium borohydride gave (*E*)-2,3-diphenylbut-2-ene-1,4-diol (**7**) as colourless prisms in 95% yield, m.p. 116—117 °C, δ(Ph) 7.30, δ(CH_2) 4.12. On the other hand, reduction of (**6a**) with lithium aluminium hydride gave (**8**), the (*Z*)-isomer of (**7**),[5] as colourless needles in 90% yield, m.p. 86.5—87.5 °C, δ(Ph) 7.03, δ(CH_2) 4.40.



(**7**)



(**8**)



$$\begin{array}{l} Ph{-}CH{-}CH_2OH \\ \quad\;\, | \\ Ph{-}CH{-}CH_2OH \end{array}$$

(**9**)

The methylene protons of (**7**) which are shielded by the phenyl rings appear at higher magnetic field than do those of (**8**). Conversely, the phenyl protons of (**8**) which are shielded by the other phenyl ring appear at higher magnetic field than do those of (**7**). Catalytic reduction of (**7**) and (**8**) over Pd–C gave *rac*-(**9**), m.p. 125—127 °C, and *meso*-(**9**), m.p. 143—144 °C,[5] respectively in almost quantitative yields.

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[†] The i.r., u.v., and n.m.r. spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$, respectively.